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Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
 Disorder in main residue
 R factor = 0.055
 wR factor = 0.169
 Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

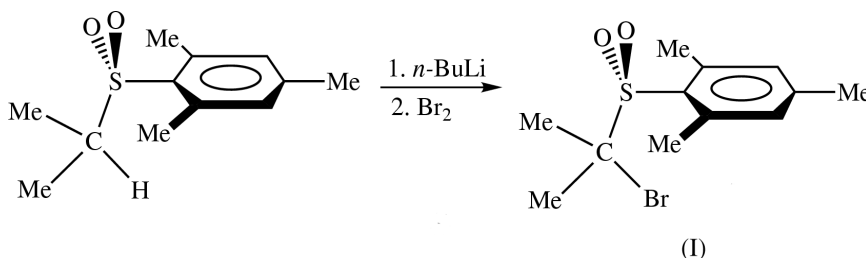
2-Bromo-2-propyl mesityl sulfone

Crystalline 2-bromo-2-propyl mesityl sulfone (α -bromoisopropyl mesityl sulfone), $\text{C}_{12}\text{H}_{17}\text{BrO}_2\text{S}$, exhibits significant rotational disorder of its α -bromoisopropyl group, although it is freely rotating in solution, as demonstrated by NMR.

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Comment

Unlike related isopropyl sulfones, 2-propyl mesityl sulfone could not be α -brominated with CBrCl_3 in powdered KOH -*tert*-BuOH, but was successfully brominated by treatment with $n\text{BuLi}$ followed by Br_2 (Chan-Yu-King, 1986), to provide 2-bromo-2-propyl mesityl sulfone, (I). In a study undertaken to determine why the initial synthetic attempt was unsuccessful (Meyers *et al.*, 1998), (I) was prepared again and its stereochemistry examined by X-ray analysis. The X-ray structure of (I) is shown with atom numbering in Fig. 1.



A salient feature of the X-ray structure resides with the significant rotational disorder of the α -bromoisopropyl group, also shown in Fig. 1. Restrained site-occupancy refinement of the six disordered sites produced the following site-occupancy values: Br1 = 0.327 (3), C11 = 0.655 (10), Br2 = 0.551 (4), C12 = 0.437 (11), Br3 = 0.105 (4), and C13 = 0.910 (11). This disorder may be associated with the small intra- and intermolecular non-bonding distances. For example, the intramolecular distances $\text{O1}\cdots\text{C8}$ and $\text{O2}\cdots\text{C7}$ are 0.45 and 0.42 \AA , respectively, less than the sum of their van der Waals radii, while $\text{C2}\cdots\text{C12}$, $\text{C6}\cdots\text{C13}$, $\text{C7}\cdots\text{C13}$ and $\text{C8}\cdots\text{C12}$ are larger by only 0.12, 0.18, 0.10 and 0.18 \AA , respectively, and the intermolecular distances $\text{O2}\cdots\text{C7}$ and $\text{O2}\cdots\text{C9}$ are larger by only 0.18 and 0.17 \AA , respectively. However, the NMR (CDCl_3) spectrum of (I) exhibits one sharp singlet (6H) for the isopropyl methyl groups.

Experimental

2-Bromo-2-propyl mesityl sulfone, (I), was prepared by treating a tetrahydrofuran solution of mesityl 2-propyl sulfone (Hua, 1979) with $n\text{BuLi}$ followed by the addition of Br_2 in hexane, as reported by Chan-Yu-King (1986) and Meyers *et al.* (1998), affording crystals (from hexanes) (m.p. 361–362 K). The m.p. and X-ray analysis of

these crystals were identical to those obtained with the crystals from an acetone solution which evaporated leaving an oil which slowly crystallized on standing.

Crystal data

$C_{12}H_{17}BrO_2S$
 $M_r = 305.23$
 Triclinic, $P1$
 $a = 9.2865$ (16) Å
 $b = 9.6572$ (18) Å
 $c = 8.2077$ (18) Å
 $\alpha = 98.813$ (18)°
 $\beta = 92.841$ (17)°
 $\gamma = 65.794$ (12)°
 $V = 663.4$ (2) Å³

$Z = 2$
 $D_x = 1.528$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 14.1$ – 14.9 °
 $\mu = 3.24$ mm⁻¹
 $T = 296$ K
 Irregular fragment, colorless
 $0.30 \times 0.22 \times 0.21$ mm

Data collection

Rigaku AFC-5S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{min} = 0.444$, $T_{max} = 0.506$
 2526 measured reflections
 2346 independent reflections
 1269 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$
 $\theta_{max} = 25.0$ °
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = 0 \rightarrow 9$
 3 standard reflections every 100 reflections
 intensity decay: 0.6%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.169$
 $S = 1.03$
 2346 reflections
 167 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 1.0978P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.66$ e Å⁻³
 $\Delta\rho_{min} = -0.61$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.037 (5)

Table 1

Selected geometric parameters (Å, °).

Br1–C10	1.895 (2)	C12–C10	1.541 (2)
Br2–C10	1.903 (2)	C13–C10	1.539 (2)
Br3–C10	1.904 (2)	S1–C10	1.756 (5)
C11–C10	1.543 (2)		
Br1–C10–C12	102.9 (9)	Br2–C10–S1	112.9 (2)
Br1–C10–C13	106.0 (5)	C13–C10–C11	103.9 (7)
Br1–C10–S1	109.4 (2)	C11–C10–S1	107.4 (6)
C13–C10–C12	104.0 (7)	Br3–C10–C11	104.7 (8)
C12–C10–S1	114.3 (10)	Br3–C10–C12	106.0 (8)
C13–C10–S1	118.7 (4)	Br3–C10–S1	116.2 (4)
Br2–C10–C11	105.6 (4)	C12–C10–C11	107.5 (10)
Br2–C10–C13	107.2 (4)		

During refinement the sum of the site-occupancy factors for the disordered Br and C sites were restrained to values of 1.0 and 2.0, respectively. Also the total site occupancy of each disordered Br/C site was restrained to 1.0. In addition, the C10–Br and C10–C distances were restrained to chemically reasonable values of 1.91 and 1.54 Å, and the C10–Br–C vectors were restrained so that they would remain relatively linear. The Br atoms were refined anisotropically, while the disordered C atoms were refined isotropically. The rotational orientation of the C7, C8, and C9 methyl groups were refined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). All H atoms were treated as riding. Although tetrahedral geometry of the α -bromoisopropyl group was not forced during the refinement, Table 1 shows that the group is relatively well behaved.

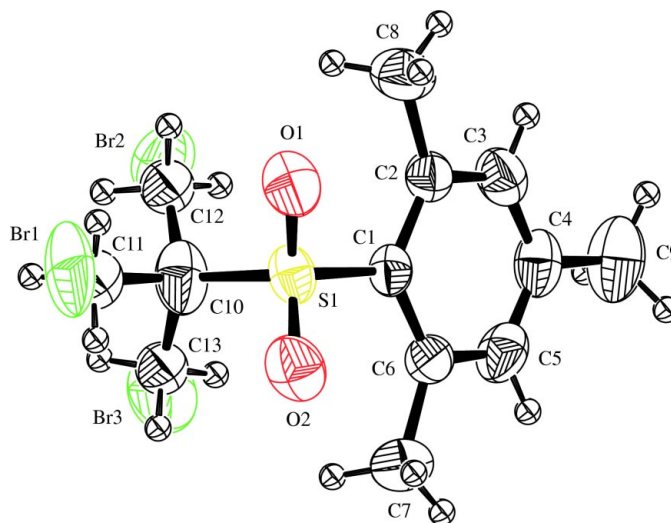


Figure 1

The molecular structure and atom-numbering scheme for (I) with displacement ellipsoids at the 50% probability level. The apparent overlap of Br1/C11 Me, Br12/C12 Me, and Br13/C13 Me, respectively, reflects the rotational disorder of the α -bromoisopropyl group.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *LS* in *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965) in *TEXSAN*; software used to prepare material for publication: *TEXSAN*, *SHELXL97*, and *PLATON* (Spek, 2000).

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